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Abstract**.** Composting is an alternative method of animal mortality disposal suitable for on-farm emergency containment of infectious diseases. Mortality composting can produce a complex variety of gases and some of them are known to be odorous. To date, relatively little is known about the makeup and temporal trends of organic gases and odors produced and emitted during composting processes. In this research, utilizing gas characterization for monitoring of the composting process was investigated. Emissions of volatile organic compounds (VOCs) and odors produced during composting of three carcass cover materials (corn stalks, oat straw and corn silage) were qualitatively studied at a laboratory scale set-up. Headspace samples were analyzed with multidimensional gas chromatography - mass spectrometry – olfactometry (MDGC-MS-O). Headspaces of decaying plant materials were tested using 85 µm Carboxen/polydimethylsiloxane (CAR/PDMS) SPME fiber. Aerobic and anaerobic conditions representing extremes of composting conditions were simulated to determine if composition of the gaseous byproducts can be used to evaluate aeration effectiveness. Volatile fatty acids (acetic, propanoic, isobutyic, butyric, isovaleric, valeric, hexanoic and heptanoic) were found as indicators of anaerobic decomposition of corn stalks and oat straw. The chemical makeup of gas and odor emissions was observed to decrease with compost age and was different for aerobic and anaerobic conditions. Chemical makeup and temporal trends in specific VOCs can be useful in non-invasive and indirect determination of the aeration status and completion of the composting process inside the biosecurity containment.

Keywords. Compost, GC-MS, GC-O, odor, SPME, VOCs.

Introduction

Composting is defined as a controlled biological process, which takes place under aerobic conditions and causes the production of simple and stable compounds through the degradation of animal and plant materials (Silvestri, et al., 1997). A wide variety of gaseous compounds are produced during this process. These include volatile fatty acids (VFAs), ammonia and other nitrogen compounds, inorganic and organic sulfur compounds, ketones, aldehydes, alcohols and terpenes (Golueke et a., 1954; Kim et al., 2005). The production of these compounds mainly depends on carbon to nitrogen ratio, oxygen concentration, substrate porosity, temperature and moisture content of the material (Keener et al., 1993).

In layered or envelope composting systems, plant residues used to cover compost materials are an important part of the composting systems. The ideal cover materials provide easily biodegradable organic material for microbial growth and gas permeable pathways within the compost material for exchange of oxygen and decomposition gases. They also retain heat, absorb excess moisture and form a barrier that helps discourage insects and scavengers (Saskatchewan Agriculture, Food and Rural Revitalization, 2005). Sawdust or fine woodchips are generally considered as some of the best plant materials due to their excellent ability to retain heat and absorb excess liquids. However they are in high demand for many other uses, making them increasingly difficult to obtain and raising their price substantially in recent years. Alternative plant materials that are much less expensive and easier to be found locally on or near livestock farms include chopped cornstalks or oat straw (Glanville et al., 2001). Microbial respiration rates of these and other plant materials including corn silage, wood shavings, alfalfa hay, soybean straw, wheat straw, large and small leaves, turkey litter, yard waste compost, beef cattle manure and sawdust have been studied by Ahn et al (2005). The highest respiration rates and heat production rates were detected for alfalfa hay, corn silage, oat straw and turkey litter, respectively. Corn stalks were reported as an acceptable cover material with a medium respiration rate. These five plant materials were suitable for mortality composting due to their high pathogenic microorganism destruction potentials (Ahn et al., 2005).

Composting operations can release gases and odor which potentially can affect air quality on local scale (Chiumenti et al., 2005). Feedstocks have potential to release several of VOCs; however, they are generally not a problem as long as certain minimum oxygen levels are met and the composting pile is capped with sufficient depth of biofiltering material to permit absorbance and break down of VOCs. Traditionally, odor evaluation involves collecting gas samples into Tedlar bags and transporting them to a laboratory for analysis by a panelist (ASTM, 1991; AVMA, 2002). Poor sample recoveries were reported for VFAs and other malodorous gases from Tedlar bags (Keener et al., 2002; Trabue et al., 2006). Also, odor detection threshold determinations (ASTM, 1991) do not provide specific chemical information needed to interpret the effects of process parameters on VOC emissions (Kim et al., 2005).

Solid phase microextraction (SPME) is an alternative sampling and sample preparation technique for quantitative air sampling (Koziel et al., 2000). Recently, SPME coupled with gas chromatography (GC) and mass spectrometry (MS) has been used to quantify VOC emissions from commercial compost samples such as biosolids, yard trimmings, animal manure and industrial by-products (Kim et al., 2002). Day et al. (1998) investigated volatile compound emissions from commercial yard waste compost using air sample collection with a syringe followed with analyses on a GC-FID. Elwell et al (2001) analyzed VFA emissions from swine manure and sawdust mixture compost utilizing Tedlar bags and GC-FID. Kim et al (2005) have reported odorous volatile compound emissions from commercial compost materials using SPME of headspace volatiles and analysis on a GC-MS. However, VOC emissions from carcass composting have not yet been studied with any sampling and analysis method. To date, relatively little is known about the makeup of organic gases and odors produced and emitted during composting processes and their temporal trends.

The long-term goal of this research project is to use specific gases produced inside such systems as indicators of compost stabilization. In this research, headspace VOCs of three carcass cover materials (corn stalks, corn silage and oat straw) were monitored for 60 days and qualitatively characterized in a laboratory setting. Plant materials were selected based on their suitability for mortality composting and abundance of these materials on a typical U.S. Midwest farm.

The objectives of the study are (i) to identify characteristic VOC and semi-VOC from each plant material in order to differentiate odorous compound emissions from plant materials and ultimately animal carcasses during mortality composting, (ii) to determine if qualitative sampling with SPME and odor detection could be useful in monitoring the effectiveness of passive aeration during the degradation of these materials and temporal variations in compost gas makeup. This study focused on the feasibility of using specific organic gases to non-invasively monitor the completion of compost process without direct visual inspection. Such a non-invasive monitoring of compost gases could be then be used for monitoring emergency mortality composts without breaching the plastic biosecurity barrier and increasing biosecurity risks.

Materials and Methods

Plant Material Collection and Preparation

Plant materials (corn stalks, corn silage and oat straw) were collected in central Iowa. The two materials with long stems (corn stalks and oat straw) were chopped to approximately 10 cm lengths. Moisture content of each plant material was measured by calculating weight loss upon drying in an oven at 75 ºC until constant weight (USCC, 2002). Moisture contents of the materials were adjusted based on the report of Ahn et al. (2005) (corn stalk: 74% w.b., corn silage: 79% w.b., oat straw: 78% w.b.) to prevent adverse effects of storage losses.

Twenty grams of samples were filled in 450 mL glass jars (Mason jars) purchased from a local market. These jars were cleaned with a laboratory-grade detergent powder and rinsed with deionized water for several times. One mm thick PTFE (polytetrafluoroethylene) liners were used to separate headspaces of the jars from their tin lids to isolate samples. Jars with their PTFE liners were placed in an oven and kept at 110 ºC overnight to drive off volatile substances and minimize potential impurities before use. Gas sampling ports were made by drilling 5 mm holes in the middle of the lids and Thermogreen half-hole septa (Supelco, Bellefonte, PA) were tightly placed in these holes. Headspaces of empty jars were collected using SPME and analyzed as a control experiment. One jar was utilized to sample headspace of each plant under aerobic and anaerobic conditions, respectively.

After filling with plant material, jars were incubated at 37 ± 1 ºC in a water bath (model Isotemp 228, Fisher Scientific, Pittsburg, PA) during experiments to encourage microbial growth (Figure 1). Temperature varies from mesophilic temperatures (10-45 ºC) to thermophilic temperatures (45-60 ºC) in typical composts. However, in this experiment, temperature was held constant to determine the effects of time on the VOC production. It is known that the efficiency of SPME extractions is reduced with higher temperatures (Pawliszyn, 1997). Thus, in this study, constant temperature was used to avoid possible reductions in extraction efficiency. Aerobic conditions were simulated by opening lids of jars for 1 min every other day during the entire 60 day trial. This passive aeration was always done after the headspace sampling to enable equilibration of VOC in the headspace during 2 day period prior to sampling. Anaerobic conditions were simulated by keeping jars closed all the time. They were assumed to be composted under anaerobic conditions after the initial few days.

Headspace SPME and Data Analysis

All headspace samples were collected using CAR/PDMS 85 µm SPME fibers and one hour sampling time. This was followed by immediate transfer of SPME fiber and insertion into the injection port of the GC and subsequent separation and identification of compounds on a multidimensional gas chromatography-mass spectrometry-olfactometry (MDGC-MS-O) system (Figure 1). At the first week of the study, headspaces of the jars were sampled every other day, since the first 7 to 10 day are known as the most active period in terms of VOC and odor production (Epstein, 1997). After the first week, samples were taken once or twice a week depending on the availability of the analytical instrument.

Chromatography and olfactometry data acquisition software consisted of MultiTrax™ V. 6.00 (Microanalytics), AromaTrax™ V. 6.61 (Microanalytics), MSD ChemStation (Agilent) and BenchTop/PBM™ V. 3.2.4 (Palisade Corporation, Ithaca, NY). Separated compounds were identified using mass spectral matches with ChemStation's NIST MS Library and PBM BenchTop MS libraries. Spectral matches and column retention times were compared with those of pure standards.

Results and Discussion

Gases and Odors Evolved During Decomposition

In the study, as many as 20 odors were detected for a particular sample (Table 1). Some of these odors were described as pleasant-to-neutral odor, e.g., sweet, medicinal and some odorants as very unpleasant odor, e.g., sewer, body odor, fecal. Potential odor control approaches could target these specific offensive odorants. The total odor was measured as the sum of products of odor intensity and odor duration for all odor and aroma events for each sample.

Selected target compounds based on their abundance in the headspace were as follows: VFAs, e.g., acetic, propanoic, 2-methylpropanoic, butanoic, 3-methylbutanoic, pentanoic, hexanoic and heptanoic acids; phenolics, e.g., phenol, 4-methylphenol, 4-ethylphenol, 2-methoxyphenol and benzeneethanol; esters, e.g., ethyl butanoate, propyl butanoate, 2-methylpropyl butanoate, butyl butanoate, ethyl caproate and 3-methylbutyl butanoate; ketones, e.g., 2-butanone and 2-heptanone; alcohols, e.g., 3-methyl-1-butanol and hexanol (Table 2). Most of these compounds were also detected in previous studies (Golueke et al., 1954; Kim et al., 2005). The abundance of target compounds were measured as the area under chromatogram peaks of characteristic single ions for each compound.

Table 1. Summary of odor character, odor intensity, odor start time, duration, and area for headspace of anaerobically composted corn silage.

Event #	Odor Descriptor	Odor Intensity (%)	Start Time (min)	Odor duration (min)	Odor Area (Intensity × width × 100)
1	Sulfury	51	1.64	0.12	610
2	Rancid, sweet	50	4.46	0.42	2,096
3	Sweet	51	6.05	0.27	1,374
4	Rancid, sweet	51	6.86	0.46	2,342
5	Sweet	41	8.62	0.29	1,187
6	Sweet	12	10.28	0.06	171
7	Ketone, sweet	61	10.89	0.62	3,775
8	Rancid	41	11.86	0.09	368
9	Sweet	50	12.61	0.17	848
10	Acid, rancid	53	12.94	0.50	2,645
11	Rancid	61	13.60	0.11	669
12	Body odor	52	14.80	0.35	1,816
13	Sewer	59	15.27	0.26	1,531
14	Body odor	89	16.33	0.36	3,198
15	Fecal	41	17.40	0.08	327
16	Rancid, foul	31	18.49	0.20	618
17	Medicinal	50	20.43	0.44	2,196
18	Acidic	40	21.79	0.12	479
19	Medicinal	51	22.90	0.34	1,731
20	Foul	41	25.11	0.32	1,309

Effects of Aeration

The abundance of all target compounds in each chemical group was summed up and presented as a function of composting time under aerobic and anaerobic conditions in Figures 1 and 2. Under anaerobic conditions, target compound emissions were always greater than emissions under aerobic conditions regardless of the plant material. High levels of VFAs, aromatics, esters, ketones and alcohols were produced under anaerobic conditions. Although fluctuations have been observed, anaerobic conditions caused more odorous compound production during the process.

Table2. Summary of selected compounds identified during composting of corn stalks, corn silage, and oat straw at both aerobic and anaerobic conditions. RT (retention time) and MS spectrum match confirmed with pure standards.

RT (min)	CAS #	Compound name	MS spectrum match (%)	Compounds detected in headspace above composted plant materials					
				Aerobic			Anaerobic		
				Corn stalks	Corn silage	Oat straw	Corn stalks	Corn silage	Oat straw
		VFAs							
13.01	64-19-7	Acetic acid	86		✓		✓	✓	✓
14.67	79-09-4	Propanoic acid	93		✓		✓	✓	✓
15.23	79-31-2	2-Methylpropanoic acid	85		✓			✓	✓
16.31	107-92-6	Butanoic acid	88		✓		✓	✓	✓
16.81	503-74-2	3-Methylbutanoic acid	72		✓		✓	✓	✓
18.24	109-52-4	Pentanoic acid	76		✓		✓	✓	✓
20.01	142-62-1	Hexanoic acid	83		✓		✓	✓	✓
21.74	111-14-8	Heptanoic acid	83						✓
		Esters							
6.11	105-54-4	Ethyl butanoate	95		✓			✓	✓
8.45	105-66-8	Propyl butanoate	76		✓			✓	✓
9.73	539-90-2	2-Methylpropyl-butanoate	76					✓	✓
10.91	109-21-7	Butyl butanoate	83		✓			✓	✓
11.10	123-66-0	Ethyl caproate	93		✓			✓	✓
12.26	109-19-3	3-Methylbutyl butanoate	83		✓			✓	✓
		Phenolics							
20.42	90-05-1	2-Methoxyphenol	93		✓			✓	
21.21	60-12-8	Benzeneethanol	94		✓			✓	✓
22.61	108-95-2	Phenol	95		✓		✓	✓	✓
23.66	106-44-5	4-Methylphenol	95		✓		✓	✓	✓
25.00	123-07-9	4-Ethylphenol	93		✓		✓	✓	✓
		Alcohols							
8.21	123-51-3	3-Methyl-1-butanol	72		✓		✓	✓	✓
11.41	111-27-3	1-Hexanol	76		✓		✓	✓	✓
		Ketones							
2.77	78-93-3	2-Butanone	50		✓		✓	✓	✓
9.08	110-43-0	2-Heptanone	88		✓		✓	✓	✓

Effects of Compost Time

Production of target gases had a consistent trend for all plant materials under both aerobic and anaerobic conditions (Figures 1 and 2). VOC production typically started at the beginning of the second week of the trial. They were not present in detectable quantities at the first week, which is not consistent with previous studies. VOC emissions were reported to be greatest during the first 9 to 10 days and greatly reduced thereafter (Krzymien et al., 1999; Epstein, 1997). In this study, delay in VOC production peak is likely due to the storage of materials prior to the experiments. Although the plant materials were stored at 4 ºC and moisture content adjustments were made before the experiments, the initial microbial decomposition during the first week might be retarded due to long storage conditions. With few exceptions, most target compounds had maximum emissions typically between weeks 2 and 5 and after the fifth week, a reduction was observed in the production of target compounds or groups of compounds. This reduction indicates compost materials started to stabilize (Haug, 1997) and monitoring gas emissions could possibly be used to monitor the completion of the process.

Effects of Utilized Plant Material

None of target compounds was found in the headspace of aerobically composted cornstalks, or oat straw. However, they were detected for the corn silage composted under aerobic conditions (Figures 1 and 2). These volatile organic compounds are intermediates in the metabolism of carbohydrates and they are accumulated in systems where oxygen is lacking Thus, the presence of these compounds in aerobically composted corn silage was not expected. They might be coming from anaerobic fermentative biodegradation that is known to occur during silage production (Kim et. al., 2005). Another reason might be anaerobic pocket formation due to less porous structure of corn silage than the cornstalks and oat straw.

The contribution of each target group (VFAs, phenolics, esters, ketones and alcohols) to the total VOC production in anaerobic treatments during the trial was compared for three plant materials in Figures 1 and 2. Volatile fatty acids contributed the largest fraction of the total VOCs for corn silage and oat straw composts. No alcohol and ester production was observed for aerobically or anaerobically composted corn stalks. Phenolic compound production was dominant for corn stalks. While nearly equal amounts of VOCs were produced during corn silage and oat straws composting, relatively lower amounts of VOC emission were detected for corn stalks. Apparent differences in the contributions of specific chemical groups to the total VOC emissions could possibly be used for the monitoring of compost processes.

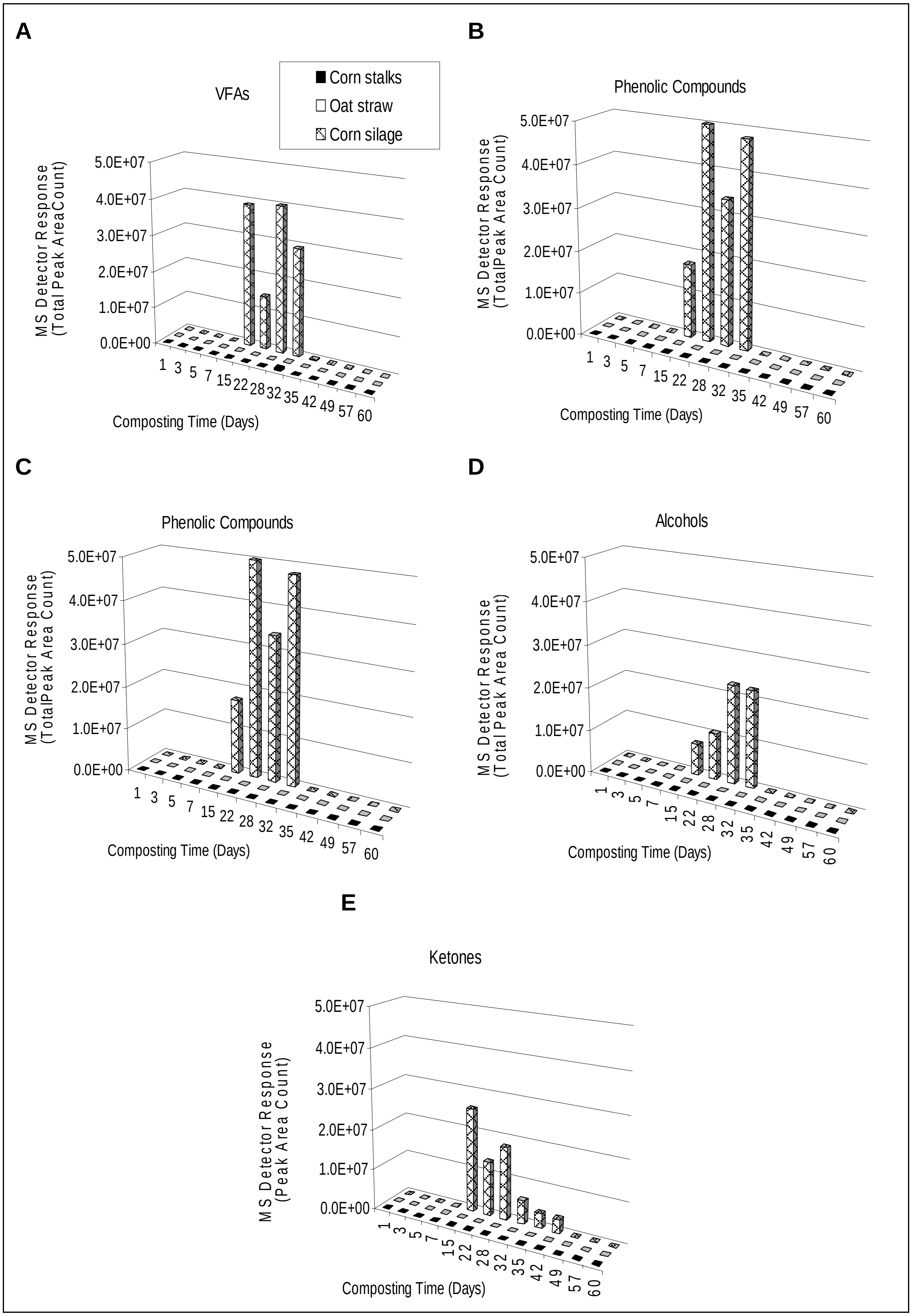

Figure 1. Comparison of VOC emissions from corn stalks, corn silage, and oat straw composts under aerobic conditions.

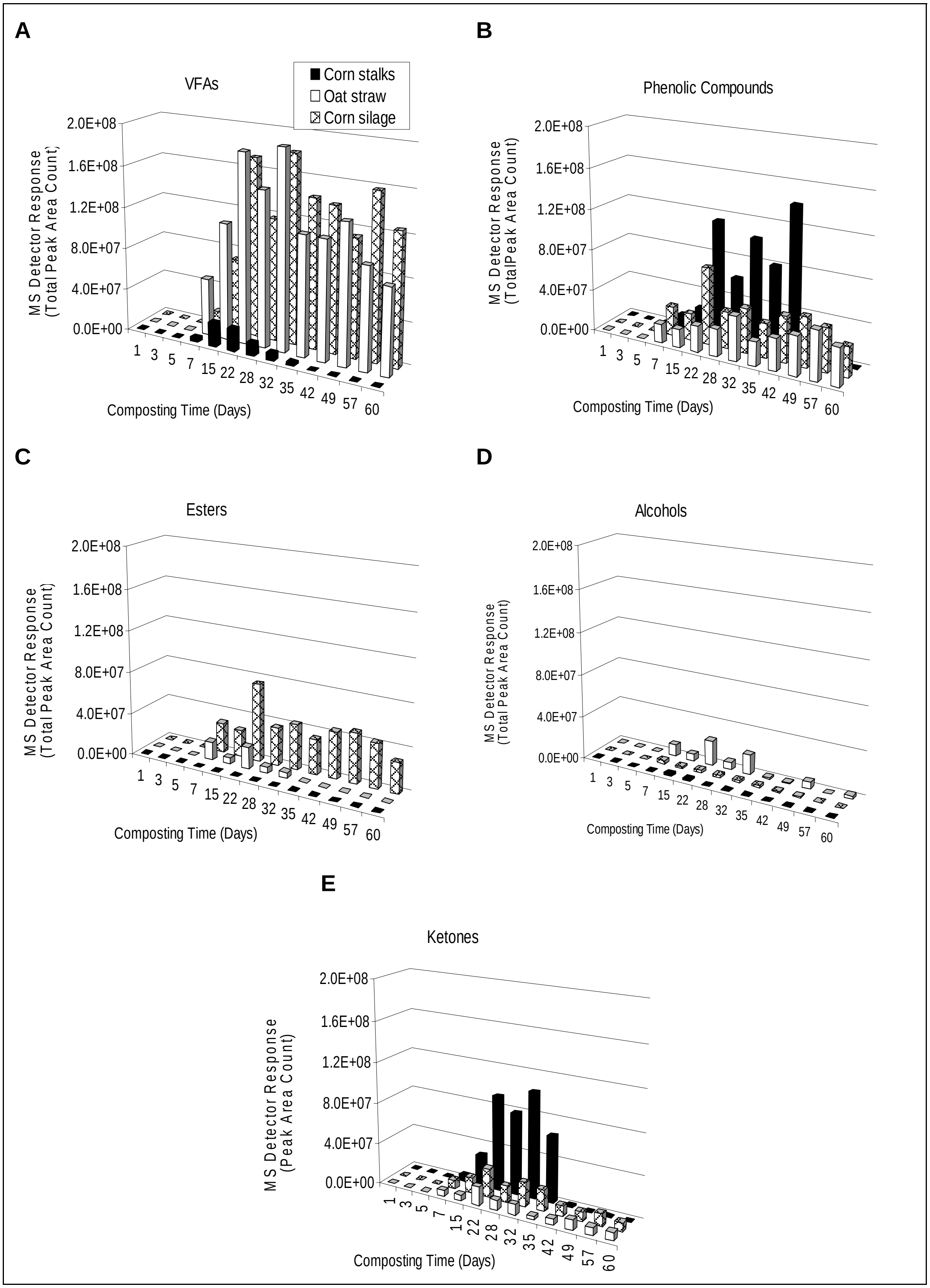

Figure 2. Comparison of VOC emissions from corn stalks, corn silage, and oat straw composts under anaerobic conditions.

CONCLUSIONS

Conclusions drawn from the study are as follows:

1. Twenty five compounds representing several chemical groups of compounds including VFAs, phenolics, esters, alcohols and ketones were consistently detected in the headspaces above the simulated compost materials.
2. Apparent differences between emissions of specific chemical groups exist for all three plant materials utilized.
3. Monitoring emissions of specific VOCs could be used to determine the status and completes of the composting process.
4. Laboratory scale experiments provided a comprehensive list of compounds for both aerobic and anaerobic composting of carcass cover materials that could be utilized to design field experiments involving SPME headspace extraction of gases emitted from real life composting processes.

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